

Single-crystal X-ray Diffraction of New Methane Hydrates

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Abstract No. shu6866

Beamline(s): X17C

Introduction: Two new types of methane hydrates (II and H) have been investigated by using synchrotron single crystal X-ray diffraction techniques with the diamond-anvil cell at room temperature. Methane hydrates are very important materials that exist in the ocean floor and in the outer planets (such as Europa). They could one day become a major energy resource. As a union of water and the simplest organic molecules, these crystals may contain secrets about life in extreme environments (including elsewhere in the solar system), and even life's origins. Being both solid- and gas-like, these materials exhibit unusual physical properties (such as very low thermal conductivity), the study of which may aid in the development of new classes of technological materials. The energy dispersive X-ray diffraction scans on the single crystal in the diamond cell were performed at the superconducting wiggler Beamline X17C of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). Single-crystal peaks were collected with an intrinsic germanium detector at $2\theta=8^\circ$ ($E_d=88.87\text{KeV}$ - Å). In this technique, a diamond cell was mounted on a goniometer with a rotation stage, allowing variation of two angles (ω and χ). Single-crystal x-ray diffraction provides unambiguous determination of structure as it resolves orientations in reciprocal space in addition to d-spacings. Overlapping lines in polycrystalline diffraction appear at entirely different points in χ - ω reciprocal space in the single-crystal diffraction. Below 200 MPa, the methane hydrate possesses the type I structure, which has an ideal composition of 5.75 water molecules to each methane molecule. Each unit cell consists of 46 water molecules and two sorts of cavities: The two small cavities are pentagonal dodecahedra (5^{12}), whereas the six large cavities are tetradecahedra ($5^{12}6^2$) having two opposite hexagonal faces and twelve pentagonal faces. The type I structure is of cubic symmetry with a space group of Pm3m, and cell parameters: $a=11.891$ (2) Å, $V=1681.3$ (5) Å³. The synthetic methane hydrate becomes the type II structure at 250 MPa. A total of 222 diffraction peaks in 49 classes were observed and the structure can be refined to a cubic unit cell of $a=17.193$ (2) Å, $V=5082.2$ (5) Å³, with a space group Fd3m. There are 136 water molecules in a unit cell of the type II structure, which also contains two types of cavities. The 16 smaller cavities are distorted pentagonal dodecahedra and the 8 large cavities are hexadecahedra ($5^{12}6^4$) having 4 hexagonal faces and twelve pentagonal faces. At 600 MPa, methane hydrate transforms to the type H structure. Seventy-nine diffraction lines in 60 classes were collected and the crystal was refined to a hexagonal system. The determined cell parameters are $a=b=11.980$ (2) Å, $c=9.992$ (3) Å, $V=1241.9$ (5) Å³, and space group is P6₃/mmc. This unit cell contains 34 water molecules. The type H structure has three different kinds of cavities: Three 5^{12} cavities, two new 12 face $4^35^66^3$ cavities, which has three squares faces, six pentagonal faces, and three hexagonal faces, and one new large $5^{12}6^8$ cavity that has twelve pentagonal faces and eight hexagonal faces. The following are single crystal X-ray diffraction patterns of type II and type H methane hydrates.

